

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
APPLICATION FOR UNITED STATES LETTERS PATENT

Title:

METHOD OF FORMING OXYNITRIDE FILM

Seung Woo Shin	Hyundaijeonjasawon Apt. 108-1107 Sadong-Ri, Daewol-Myun, Ichon-Shi, Kyungki-Do Republic of Korea
Cha Deok Dong	Dongyang Apt. 101-704, 322, Songjung-Dong, Ichon-Shi Kyungki-Do Republic of Korea

# METHOD OF FORMING OXYNITRIDE FILM

## BACKGROUND OF THE INVENTION

### 5 Field of the Invention

The present invention relates to a method of fabricating semiconductor devices, and more particularly, to an oxynitride film.

### Background of the Related Art

10 A silicon oxide film (hereinafter called 'pure silicon oxide film') in which a silicon substrate is oxidized within the oxidization furnace using a mixed gas of an oxygen ( $O_2$ ) gas or  $H_2O$  and  $O_2$  has been used as a tunnel oxide film of the flash memory device. As the effective thickness of the tunnel oxide film required along with micronization of the device is reduced,  
15 however, it becomes difficult to satisfy the characteristic of the film required in the device with only the characteristic of the pure silicon oxide film.

Meanwhile, if the pure silicon oxide film is replaced by the oxynitride film, it is possible to secure characteristics of the film that were not satisfied by the pure silicon oxide film (for example, stress induced leakage current, the  
20 electric charge necessary for breakdown, the life of the film, etc.). This oxynitride film may be fabricated by a method by which the pure silicon oxide film of a give thickness is grown and a nitrification process is then implemented using  $NH_3$ ,  $N_2O$ ,  $NO$ , or the like to form a thin nitrogen layer at the existing silicon (Si)-silicon oxide ( $SiO_2$ ) film interface or a nitrogen-rich

oxide film. If the nitrogen layer is formed at the Si-SiO<sub>2</sub> interface by this method, the intrinsic properties of the film itself are improved but the concentration of the trap charge is increased in proportion to the concentration of nitrogen. For this reason, the carrier mobility in the channel of the transistor formed underlying it is influenced to change the threshold voltage of the transistor.

In particular, in case of NMOS, if the oxynitride film is used as the tunnel oxide film, the threshold voltage is dropped over 100mV compared with the pure silicon oxide film even where the concentration of nitrogen at the Si-SiO<sub>2</sub> interface is 1atom%. This, it is difficult to secure the transistor characteristic. FIG. 1 is a graph illustrating the difference in the threshold voltage at the transistor using the pure silicon oxide film and the oxynitride film as the dielectric film. In FIG. 1, 'a' indicates a case where the pure silicon oxide film is used as the dielectric film, and 'b' and 'c' indicate cases where the oxynitride film is used as the dielectric film. From FIG. 1, it could be seen that if the oxynitride film is used as the tunnel oxide film, the threshold voltage is dropped about 110mV compared with the pure silicon oxide film when the concentration of nitrogen at the Si-SiO<sub>2</sub> interface is dropped about 1.437atom%.

20

### **SUMMARY OF THE INVENTION**

Accordingly, the present invention is contrived to substantially obviate one or more problems due to limitations and disadvantages of the related art.

An object of the present invention is to provide a method of forming an

oxynitride film capable of securing the characteristics of a film that are significantly improved than the characteristics of a film obtained in a pure silicon oxide film and minimizing variation in the threshold voltage of a transistor by a trap charge.

5 Additional advantages, objects, and features of the invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure  
10 particularly pointed out in the written description and claims hereof as well as the appended drawings.

To achieve these objects and other advantages and in accordance with the purpose of the invention, as embodied and broadly described herein, a method of fabricating an oxynitride film according to the present invention is  
15 characterized in that it comprises the steps of loading a silicon substrate into an oxidization furnace, implanting an oxygen based source gas into the oxidization furnace to grow a pure silicon oxide film on the silicon substrate, blocking implantation of the oxygen based source gas and implanting an inert gas to exhaust the oxygen based source gas remaining within the oxidization  
20 furnace, raising a temperature within the oxidization furnace to a nitrification process temperature, stabilizing the temperature within the oxidization furnace, implementing a nitrification process for the pure silicon oxide film by implanting a nitrogen based source gas, and stopping implantation of the nitrogen based source gas and rapidly cooling the oxidization furnace while

implanting the inert gas into the oxidization furnace.

In another aspect of the present invention, it is to be understood that both the foregoing general description and the following detailed description of the present invention are exemplary and explanatory and are intended to  
5 provide further explanation of the invention as claimed.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

The above and other objects, features and advantages of the present invention will be apparent from the following detailed description of the  
10 preferred embodiments of the invention in conjunction with the accompanying drawings, in which:

FIG. 1 is a graph illustrating the difference in the threshold voltage at a transistor using a pure silicon oxide film and an oxynitride film as a dielectric film;

15 FIG. 2 illustrates that a silicon oxide ( $\text{SiO}_2$ ) film is formed on a silicon substrate;

FIG. 3 illustrates that nitrogen is stably substituted at a Si-SiO<sub>2</sub> interface by implementing a nitrification process;

FIG. 4 illustrates that a trap charge is formed at a Si-SiO<sub>2</sub> interface after  
20 a nitrification process; and

FIG. 5 illustrates that the trap charge is removed and nitrogen is stably substituted after an annealing process.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

FIG. 2 illustrates that a silicon oxide ( $\text{SiO}_2$ ) film is formed on a silicon substrate, FIG. 3 illustrates that nitrogen is stably substituted at a Si-SiO<sub>2</sub> interface by implementing a nitrification process, FIG. 4 illustrates that a trap charge is formed at a Si-SiO<sub>2</sub> interface after a nitrification process, and FIG. 5 illustrates that the trap charge is removed and nitrogen is stably substituted after an annealing process.

Referring now to FIG. 2 ~ FIG. 5, the reason why the density of the trap charge is increased as the concentration of nitrogen at the Si-SiO<sub>2</sub> interface is increased is that an interfacial trap charge is generated due to stress occurring while Si-N bonding in lieu of Si-O bonding is formed at the Si-SiO<sub>2</sub> interface by nitrogen penetrated into a pure silicon oxide film in a nitrification process. Accordingly, in order to minimize the trap charge of the Si-SiO<sub>2</sub> interface, a method capable of reducing by stress occurring while nitrogen is coupled with silicon and oxygen at the Si-SiO<sub>2</sub> interface must be sought. In order to solve the above problem, the present invention employs a method of relaxing stress by controlling an annealing process condition during the nitrification process or implementing a subsequent annealing process after the nitrification process.

#### <Embodiment 1>

A method of controlling the annealing process condition during the nitrification process will be first described.

Turning to FIG. 2 and FIG. 3 again, in order to relax stress occurring

when nitrogen is injected into the Si-SiO<sub>2</sub> interface, it is required that a temperature higher than 950°C being a viscous flow temperature of the SiO<sub>2</sub> film be kept. If the nitrification process is implemented over this temperature, stress is relaxed due to the mobility of the SiO<sub>2</sub> film although  
5 nitrogen is substituted in the Si-O bonding, so that generation of the trap charge is fundamentally prevented. Meanwhile, if only NH<sub>3</sub>, N<sub>2</sub>O or NO is used as a source gas when the nitrification process is implemented at high temperature of over 950°C, it would be difficult to implant the amount of nitrogen corresponding to the concentration that is expected for the Si-SiO<sub>2</sub>  
10 interface or control the thickness of a nitrogen-rich oxide film. This problem could be solved by mixing argon (Ar) being an inert gas or N<sub>2</sub> gas with a source gas in an adequate ratio and then implanting the mixture. This will be described in more detail below.

A pure silicon oxide film of a desired thickness is first grown within the  
15 oxidization furnace. At this time, the pure silicon oxide film may be formed by means of a wet oxidization process at a temperature of about 750~800°C. After the oxidization process, the source gas is blocked and the inert gas is injected into the oxidization furnace to exhaust all the remaining oxide materials. In succession, in a state that growth of an unwanted oxide film is  
20 prevented under the inert gas atmosphere, the temperature is raised higher than 950°C in order to implement the nitrification process. If the temperature for implementing the nitrification process is stabilized, the nitrification process is implemented by injecting the source gas into the oxidization furnace. At this time, the source gas used may include NH<sub>3</sub>, N<sub>2</sub>O, NO, or the like. Also,

it is possible that the source gas is diluted with the inert gas such as argon (Ar) or N<sub>2</sub> in order to grow an oxide film having the concentration of nitrogen required for the Si-SiO<sub>2</sub> interface and a nitrogen-rich oxide film.

After the nitrification process is completed, in a state that the source gas  
5 is blocked and only a pure inert gas is injected into the oxidization furnace, the oxidization furnace is cooled as fast as it is. The cooling speed at this time is good if it is fast as soon as possible, which does not cause a physical bent phenomenon in the wafer. As the cooling speed of the oxidization furnace is fast, it is effective to prevent reproducibility of the trap charge. At this time,  
10 after the pure silicon oxide film is grown in the oxidization furnace if necessary for process constitution, the nitrification process may be implemented in additional equipment in the above procedure.

#### <Embodiment 2>

A method of implementing a subsequent annealing process after the  
15 nitrification process will be described.

Turning to FIG. 4 and FIG. 5, in a method of removing the trap charge already occurred in the nitrification process through subsequent annealing, if the annealing process is implemented by implanting the inert gas (for instance, Ar, N<sub>2</sub>, etc.) at a temperature of over a nitrification process temperature, the  
20 Si-SiO<sub>2</sub> interface having a unstable lattice structure due to nitrogen substitution is reconstructed to have a stable lattice structure, so that the trap charges that were already generated are extinguished.

This will be described in more detail below.

A pure silicon oxide film of a desired thickness is first grown within the



oxidization furnace. At this time, the pure silicon oxide film may be formed by implementing a wet oxidization process at a temperature of about 750~800°C. After the oxidization process, a source gas is blocked and an inert gas is injected into the oxidization furnace to exhaust all the remaining  
5 oxide materials. In succession, in a state that growth of an unwanted oxide film is prevented under the inert gas atmosphere, the temperature is stabilized for performing a nitrification process. At this time, the nitrification process temperature has no limitation to the lowest temperature unlike the first embodiment and would be okay if it is sufficient to secure a desired  
10 nitrification process level. In general, it would be possible if the temperature is over 800°C. After the temperature for the nitrification process is stabilized, a nitrification process is implemented by implanting the source gas into the oxidization furnace. At this time, the source gas used may include NH<sub>3</sub>, N<sub>2</sub>O, NO, or the like. Also, it is possible that the source gas is diluted with  
15 the inert gas such as argon (Ar) or N<sub>2</sub> in order to grow an oxide film having the concentration of nitrogen required for the Si-SiO<sub>2</sub> interface and a nitrogen-rich oxide film.

After the nitrification process is completed, the temperature is raised up to an annealing process temperature in a state that the source gas is blocked  
20 and only a pure inert gas is implanted into the oxidization furnace. At this time, the temperature of the annealing process has no problem if it is performed at a temperature of over the nitrification process temperature. Although the effect of removing the trap charge is outstanding as the temperature is kept high, the temperature is adequately controlled considering

a thermal budget affecting the device. The annealing process is implemented under an inert atmosphere such as argon (Ar) or N<sub>2</sub>. After the process is completed, the oxidization furnace is cooled at a speed as fast as possible. The cooling speed at this time is good if it is fast as soon as possible, which does not cause a physical bent phenomenon in the wafer. As the cooling speed of the oxidization furnace is fast, it is effective to prevent reproducibility of the trap charge. At this time, after the pure silicon oxide film is grown in the oxidization furnace if necessary for process constitution, the nitrification process may be implemented in additional equipment in the above procedure.

As described above, according to the present invention, the method of forming the oxynitride film proposed by the present invention can be applied to fabricate the tunnel oxide film of the flash memory device or a gate oxide film of other memories or logic devices. In this case, the present invention can have new effects that it can secure the characteristics of a film that are significantly improved than those obtained in the conventional pure silicon oxide film, and minimize variation in the threshold voltage of the transistor by a trap charge that is a disadvantage in the existing oxynitride film.

The forgoing embodiments are merely exemplary and are not to be construed as limiting the present invention. The present teachings can be readily applied to other types of apparatuses. The description of the present invention is intended to be illustrative, and not to limit the scope of the claims. Many alternatives, modifications, and variations will be apparent to those skilled in the art.